Preparation and transport properties of non-hydrated Na$_{0.5}$CoO$_2$ single crystals

X. Z. Chen [a], Z. A. Xu [a,*], G. H. Cao [a], J. Q. Shen [a],
L. M. Qiu [b], and Z. H. Gan [b]

[a]*Department of Physics, Zhejiang University, Hangzhou 310027, P. R. China*

[b]*Institute of Refrigeration and Cryogenic Engineering, Zhejiang University,
Hangzhou 310027, P. R. China*

Abstract

Single crystals of Na$_{0.5}$CoO$_2$ were obtained through a flux method followed by de-intercalation of sodium. The Na$_{0.5}$CoO$_2$ samples were found to be vulnerable to water in the air and a hydration process in which H$_2$O molecules fill oxygen vacancies in CoO$_2$ layers is suggested to be responsible for the unusual vulnerability to water. The transport properties, including resistivity (ρ), thermopower (S) and Hall coefficient (R_H), were studied in a temperature range of 5-300 K. The compound shows a weak localization of carriers just below 200 K and Co^{3+}-Co^{4+} charge ordering at about 30 K, a relatively lower temperature than previously reported. The results seem to be quite different from those previously reported for this system [Foo et al, Phys. Rev. Lett. 92 (2004) 247001]. Possible mechanism underlying this kind of inconsistency is discussed.

Layered transition-metal oxide Na$_x$CoO$_2$ has attracted great interest for its unusual behaviors due to strongly correlated electrons in the past years. It has a crystal structure consisting of layers of edge shared CoO$_6$ octahedra, between which Na$^+$ ions are inserted. Early researches have found an unusually large thermoelectric power with Na content x=2/3 [1]. Spin entropy carried by holes (Co^{4+}) hoping in a Co^{3+} background has been regarded as the likely source of enhanced thermopower [2]. Recently, superconductivity with a transition

---

* Corresponding author
Email address: `zhuan@css.zju.edu.cn` (Z. A. Xu).

temperature T_c of about 5 K has been found in water-intercalated compound $Na_{0.35}CoO_2$-$1.3H_2O$ [3], which has been viewed as a breakthrough in search of exotic superconductors other than the copper oxides. Magnetic susceptibility studies [4,5] have showed that $Na_{0.35}CoO_2$-$1.3H_2O$ is an extreme type II superconductor, just like high T_c cuprates, and extensive Co NMR/NQR studies [6,7,8] have shown evidences for non-s-wave superconductivity. Besides the large thermopower and superconductivity, very recent research [9] found that as the sodium concentration x increases from 0.30 to 0.75, non-hydrated Na_xCoO_2 goes from a paramagnetic metal to a charge ordered insulator (at x=0.5), and then to a Curie-Weiss metal. The sudden appearance of charge ordered state and unusual transport properties of $Na_{0.5}CoO_2$ have made it a focus of attention. The distinct properties of this compound have been determined to be related to the Na^+ ion-vacancy ordering and consequential Co^{3+}-Co^{4+} charge ordering at low temperature.

In this paper, we prepared Na_xCoO_2 crystal samples with x=0.5 and studied the transport properties including resistivity, thermopower and Hall coefficient. The samples were found to be vulnerable to the water in the air and the reaction between crystals and water seemed to bring significant influence on transport properties of the samples. Furthermore, our results on the temperature dependence of thermopower, magnetic susceptibility and Hall coefficient were found quite different from those in Ref.[9], which may throw further complications on this compound.

The starting crystals of Na_xCoO_2 were grown by a flux method following the procedure reported in Ref. [10]. To remove Na content , the as-grown crystals were immersed in solutions obtained by dissolving different amounts I_2 in acetonitrile. After reacting for a month at ambient temperature, the samples were washed several times with acetonitrile and then dried. The crystal structure was characterized by X-Ray Diffraction (XRD). The measurements of in-plane electrical resistivity ρ, thermopower S, Hall coefficient R_H and magnetic susceptibility M were carried out using a Quantum-Design PPMS-9 system. Unless mentioned otherwise, the transport measurements were performed just after preparation procedure and different measurements of a sample were taken as soon as possible to ensure uniformity of the sample.

Fig. 1 shows the typical XRD patterns for the as-grown crystal (a) and for de-intercalated crystal (b). From these patterns, the crystals are considered to be of single phase. The Na content x of starting crystals was determined to be 0.75 from the c-axis parameter, using the calibration of the relationship between c-axis parameter and Na content reported in Ref [9]. Na_xCoO_2 crystals with x content near 0.5 can be easily obtained by de-intercalation using I_2-CH_3CN solution with excess I_2 concentrations for 30 days. The long reaction time assures the uniformity of Na content of de-intercalated crystals. It should be mentioned that so long as there is enough I_2 in the solution, the Na
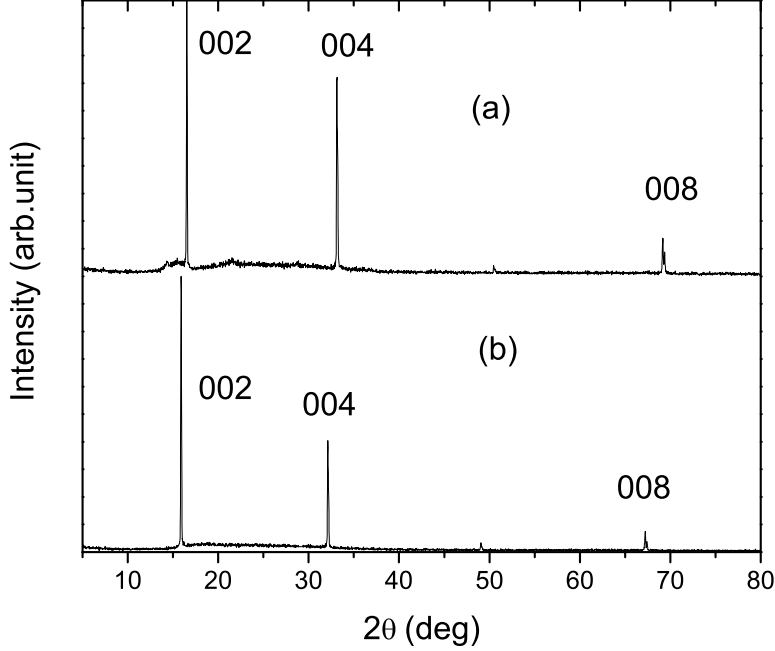
Fig. 1. XRD patterns (Cu K radiation) for Na_xCoO_2 crystals. (a) As-grown crystals $Na_{0.75}CoO_2$, (b) de-intercalated crystal $Na_{0.5}CoO_2$.

content x of de-intercalated crystals is always near 0.5 despite the different I_2 concentrations, which means that formation of the composition with x near 0.5 is favored during the de-intercalation of Na.

Na_xCoO_2 samples with low Na content ($x < 0.35$) are easy to absorb water in the atmosphere and form hydrated Na_xCoO_2-yH_2O with H_2O molecules being inserted between CoO_2 layers. However, when x comes as high as 0.45, the inserting of inter-layer H_2O is not favored [11]. Meanwhile, our results show that $Na_{0.5}CoO_2$ samples are vulnerable to the small content of water in air. We have studied the time dependence of resistivity of $Na_{0.5}CoO_2$ samples preserved in dry air as well as humid air, as shown in Fig. 2. The original samples (Sample A) were newly obtained by de-intercalation process mentioned above, with c-axis lattice constant of 11.131 Å, for which Na content x was estimated to be near 0.50. After each measurement, the samples were preserved in dry air (cabinet with humidity 35%, Sample B, C, D) and humid air (Sample E). As can be seen from Fig. 2 (a), the fresh samples (Sample A) show a transition below 50 K and the resistivity increases quickly after this transition (The detailed behaviors of fresh samples will be discussed below). The transition broaden and becomes less evident and finally unobservable after the samples were kept in air for a long period of time, which is shown in Fig. 2 (a) for Sample B, Sample C and Sample D. The same variation of resistivity occurs much

more rapidly when the samples were put in humid air (Fig. 2 (b), Sample E). Sample F and G were obtained by annealing Sample E at $100\,°C$ and $250\,°C$ respectively for an hour, and their resistivity curves were shown in Fig. 2(b). It is very interesting that Sample F (annealed at $100\,°C$) shows little difference in resistivity with Sample E while Sample G has almost the same behaviors in resistivity as Sample A, which means sintering at $250\,°C$ has restore Sample E to its original state (Sample A). It should be mentioned that, according to our XRD studies, no observable structural changes corresponding to this resistivity variation can be found and all the samples remain single phase.

To give further insight into this process, we combined thermogravimetric (TG) and differential-thermal-analysis (DTA) studies with resistivity measurements. Fig. 3 shows TG and DTA curves for Samples E. From Fig. 3, two weight losses can be observed, one below $100\,°C$ and one at about $245\,°C$, and the later is accompanied by a negative peak in DTA curve. The first weight loss below $100\,°C$ may come from the release of water absorbed on the surface of samples and it makes no contribution to the variation in resistivity. We believe that the weight loss at $245\,°C$ is responsible for all resistivity variations. According to some previous reports on superconducting $Na_xCoO_2 - yH_2O$, intercalation of water between CoO_2 layers will increasingly separate neighboring layers and thus affect resistivity [12]. This part of water will lose quickly when samples were put in dry even at room temperature and resistivity is restored [12]. However, it's quite different in our case. First, the small portion of water accounting for resistivity variations in our samples will not be released from the sample until $245\,°C$, a much higher temperature than the usual temperature for releasing inter-layered water. Second, only a very small proportion of water (about 0.015 H_2O per formula unit estimated from the weight loss at $245\,°C$) can be absorbed into crystals even when they are put in humid atmosphere for a long time. Third, no structural changes were observed from XRD studies in spite of dramatic changes in resistivity. All these differences make the hydration process seem complicated. One of the probable mechanisms is that H_2O molecules are scattered in CoO_2 layers instead of being inserted between them [13]. In such model, the O^{2-} ions of H_2O fill the oxygen vacancies in CoO_2 while leaving H^+ suspended. If this is the truth, only a small portion of water depending on the density of O^{2-} vacancies can be absorbed and definitely it will modify the periodic potential, have influence on the Na^+ ion-Na vacancy ordering and consequently contribute to transport properties of the system. The density of O^{2-} vacancies in CoO_2 layers can be created during de-intercalation of Na content [14], depending on the preparation process. The special vulnerability of $Na_{0.5}CoO_2$ samples to water makes consistent studies on this system difficult, for instance, special care is required to preserve samples and all measurements should be taken as soon as possible to assure the uniformity of test samples.

The transport measurements of $Na_{0.5}CoO_2$, including resistivity ρ, Hall co-
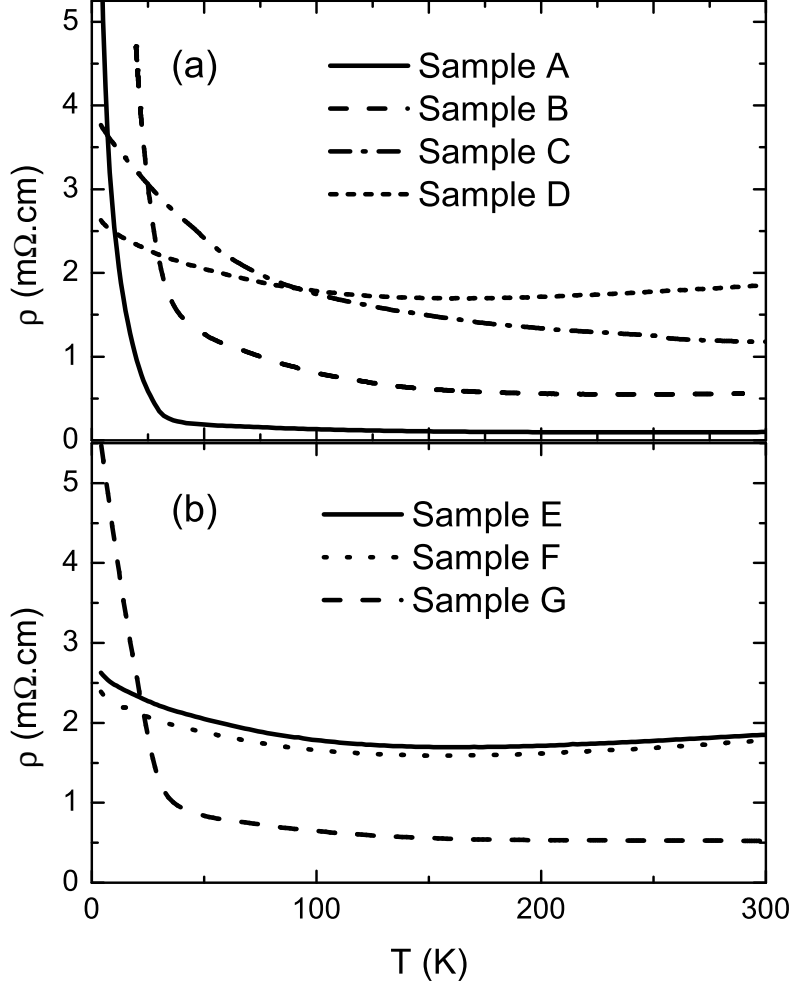
Fig. 2. Temperature dependence of resistivity for $Na_{0.5}CoO_2$ crystals with different water content. Sample A: newly prepared samples(no water content), Sample B: expose Sample A to dry air for 40 days, Sample C: expose Sample A to dry air for 80 days, Sample D: expose Sample A to dry air for 300 days, Sample E: expose Sample A to humid air for 5 hours, Sample F: anneal Sample E at 100 °C for an hour, Sample G: anneal Sample E at 250 °C for an hour. All the samples are of single phase, and no structural differences between samples can be observed from XRD studies.

efficient R_H, thermopower S and magnetic susceptibility M/H were carried out in newly prepared sample (Sample A) in a temperature range of 5-300 K. Fig. 4 shows the in-plane resistivity ρ and Hall coefficient R_H, and Fig. 5 shows thermopower S and magnetic susceptibility M/H (H∥c =1 T) as a function of temperature. ρ and R_H show quite similar temperature dependence. They both decreases gradually while temperature drops from room temperature. However, below 200 K, they start to increase slowly (see the enlargement of
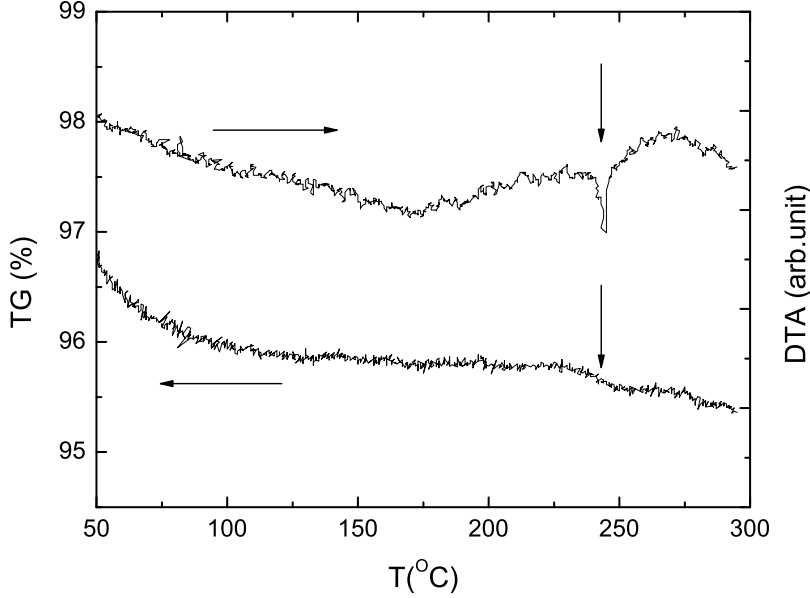
Fig. 3. TG and DTA curves for water-incorperated $Na_{0.5}CoO2$ sample (Sample E). The arrows show the water loss at about 245 °C.

ρ-T curve in the inset of Fig.4). Correspondingly, S starts to decrease below 200K, as shown in Fig.5. A sharp transition in transport properties can be observed at about 30 K. Below 30 K, the increasing trend of ρ and R_H become much rapid, associated with a quick increase in M which is similar to the result reported in Ref. [16]. S drop linearly to zero below 30 K (Fig.5). There is a tiny cusp below 50 K in magnetic susceptibility and no anomaly can be seen around 88 K.

According to previous study [9,15], superlattice of ordered Na^+ ion-Na vacancy has been observed by electron diffraction in $Na_{0.5}CoO_2$ even at room temperature and the long-range ordering of Na^+ ion-vacancy at low temperature are suggested for this compound by thermal conductivity measurement. We presume that the changes starting around 200 K in ρ, R_H and S result from the ordering of Na^+ ion-vacancy. The ordering of Na^+ ion-vacancy introduces potential fluctuation which modulates electronic state and consequently leads to Co^{3+}-Co^{4+} charge ordering in CoO_2 conduction layers. In our case, the Hall density at 100 K for $Na_{0.5}CoO_2$ is 40 times smaller than that for $Na_{0.75}CoO_2$(not shown in the paper). Below 30 K, ρ, R_H and M start to grow quickly, these may come from Co^{3+}-Co^{4+} charge ordering transition.

However, there are many apparent differences between our results and those reported in Ref. [9]. First, no evident transition in R_H or S at 87 K is observed from our results. Second, the sharp transition in ρ in our case is around 30 K,
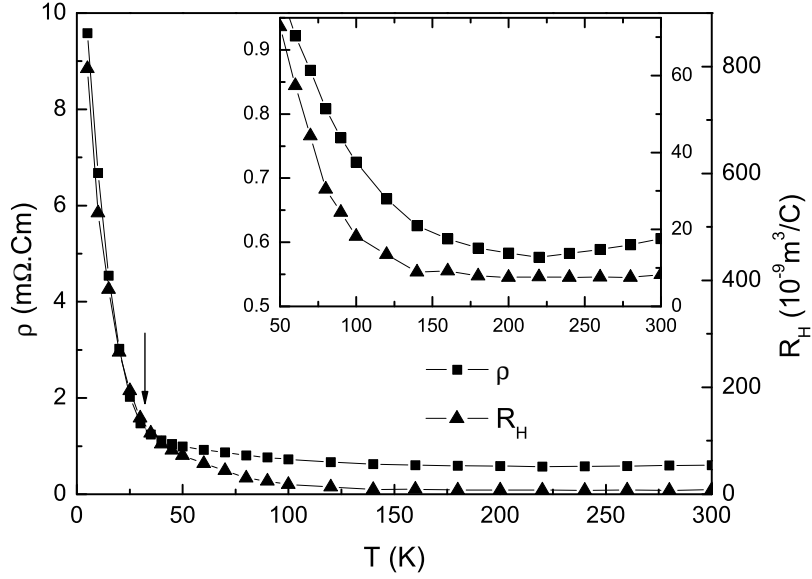
6

Fig. 4. Temperature dependences of in-plane resistivity ρ and Hall coefficient R_H for $Na_{0.5}CoO_2$. The arrow show the transition at about 30 K. Inset is the enlarged plot for $T \geq 50$ K.
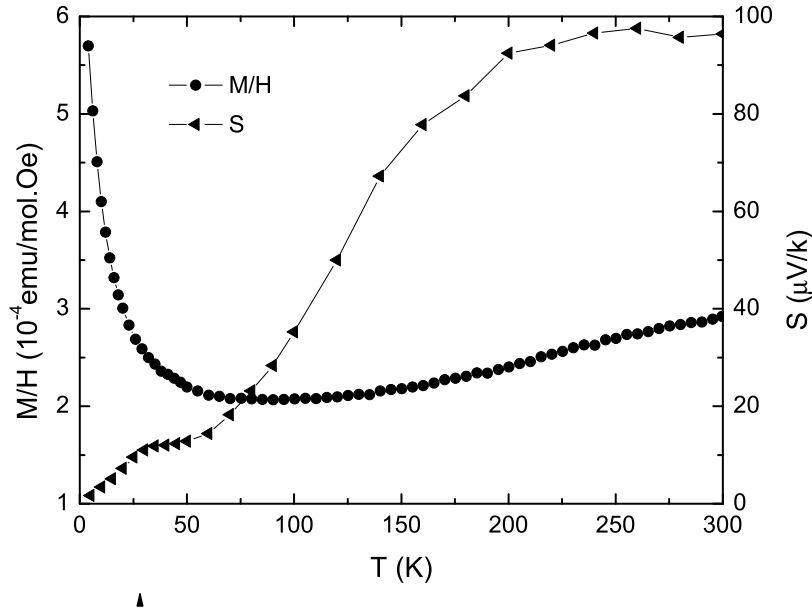

Fig. 5. Temperature dependences of thermopower S and magnetic susceptibility M (H ∥ c) for $Na_{0.5}CoO_2$. The arrow shows the transition at 30 K .

while a sharp transition in ρ at 53 K is observed in Ref. [9]. And third, the system in Ref [9] shows evidence for electron-hole symmetry (Both S and R_H fall toward zero as $T \rightarrow 0$), while in our case the system remains hole-like in the whole temperature investigated and Hall density ($1/eR_H$) instead of R_H goes to zero as $T \rightarrow 0$. It should be noted that the behaviors of resistivity, thermopower and Hall coefficient of our parent crystals (x=0.75) are very similar to the those reported in Ref. [9] (not shown here). Therefore the above differences for the samples with x=0.5 seem to be surprising. Recalled that the $Na_{0.5}CoO_2$ crystals are vulnerable to water, we suggested that the oxygen vacancies in the CoO_2 layers could account for these differences. For the ideal composition of Na_xCoO_2 with x=0.5, the ratio of Co^{3+}/Co^{4+}(eletron/hole) is 1. If a certain amount of oxygen vacancies are introduced into the CoO_2 layers during preparing process(this is quite likely to happen in $Na_{0.5}CoO_2$), it will destroy not only the electron-hole symmetry, but also translation symmetry of the periodic potential. Thus, we can expect that even a small number O^{2-} vacancies will have great influence on the transport properties of the system. This is supported by the result that only 0.015 H_2O per formula unit filling into O^{2-} vacancies will substantially change the resistivity of the system.

In summary, the single crystals of $Na_{0.5}CoO_2$ were prepared and the transport properties were investigated. The unusual vulnerability of the sample to water in the air was found and may result from filling oxygen vacancies in CoO_2 layers with H_2O molecules. The temperature dependence of resistivity, Hall coefficient, and thermopower shows a weak localization of carriers just below 200 K and Co^{3+}-Co^{4+} charge ordering at about 30 K, a relatively lower temperature than previously reported. The differences in transport properties between our results and those reported in Ref. [9] may be caused by the oxygen vacancies in CoO_2 layers. More studies are needed to discover the underlying mechanism for the novel transport properties of this system.

References

[1] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B 10 (1997) 12685.

[2] Y.Y. Wang , N.S. Rogabo, R.J. Cava and N.P. Ong, Nature 423 (2003) 425.

[3] K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R.A. Dilanian and T. Sasaki, Nature 422 (2003) 53.

[4] G.H. Cao, C.M. Feng , Y. Xu, W. Lu, J.Q. Shen, M.H. Fang and Z.A. Xu, J. Phys: Condens. Matt. 15 (2003) 519.

[5] H. Sakurai, K. Takada, S. Yoshii, T. Sasaki, K. Kindo and E. Takayama-Muromachi, Phys. Rev. B 68 (2003) 132507.

[6] Y Kobayashi, M Yokoi and Sato, J. Phys. Soc. Jpn., 72 (2003) 2161.

[7] K. Ishida, Y. Ihara, Y. Maeno, C. Michioka, M. Kato, K. Yoshimura, K. Takada, T. Sasaki, H. Sakurai and E. Takayama-Muromachi, J. Phys. Soc. Jpn. 72 (2003) 3041.

[8] T. Fujimoto, G. Zheng, Y. Kitaoka , R.L. Meng , J. Cmaidalka and C.W. Chu, Phys. Rev. Lett. 92 (2004) 047004.

[9] M. L. Foo, Y. Y. Wang, S. Watauchi, H.W. Zandbergen, T. He, R.J. Cava and N.P. Ong, Phys. Rev. Lett 92 (2004) 247001.

[10] M. Mikami, M. Yoshimura, Y. Mori, T. Sasaki, R. Funahashi and I. Matsubara, Jpn. J. Appl. Phys. 41 (2002) 777.

[11] R.E. Schaak, T. Klimczuk, M.L. Foo and R.J. Cava, Nature 424 (2003) 527.

[12] M.L. Foo, R.E. Schaaka, V.L. Millera, T. Klimczuk, N.S. Rogadoa, Y. Wang, G.C. Laua, C. Craleya, H.W. Zandbergen, N.P. Ong, and R.J. Cava, Solid State Communications 127 (2003) 33.

[13] F. Rivadulla, J.S. Zhou and J. B. Goodenough, Phys. Rev. B 68 (2003) 075108.

[14] K. Maarit, A.Isao, M. Teruki, and Y. Hisao, Chem. Mater. 16 (2004) 1693.

[15] W. Zandbergen, M.L. Foo, Q. Xu, V. Kumar and R.J. Cava, Preprint, cond-mat/0403206.

[16] F. C. Chou, J. H. Cho, and Y. S. Lee, Preprint, cond-mat/0404061.